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Monodispersed Spherical Colloids of Se@CdSe: Synthesis and Use as Building Blocks in Fabricating Photonic Crystals

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ABSTRACT

Monodispersed spherical core–shell colloids of Se@Ag_2Se have been exploited as a chemical template to synthesize Se@CdSe core–shell particles using a cation-exchange reaction. A small amount of tributylphosphine could facilitate the replacement of Ag^+ by Cd^{2+} in methanol at 50 °C to complete the conversion within 150 min. The orthorhombic structure of β-Ag_2Se changed to a well-defined wurtzite lattice for CdSe. The CdSe shells could be converted back to β-Ag_2Se by reacting with $AgNO_3$ in methanol at room temperature. Because of the uniformity in size and high refractive index associated with the Se@CdSe core–shell colloids, they could serve as a new class of building blocks to fabricate photonic crystals with wide and strong stop bands.

Monodispersed spherical colloids have attracted extensive attention because of their use as the building blocks for self-assembly to fabricate 3D photonic crystals.[1] Colloids made of polymers or silica have been the main focus so far despite their intrinsic limit in refractive index contrast.[2] The high refractive indices of inorganic semiconductors may provide some immediate advantages over conventional dielectric materials and possibly lead to the formation of wider (even complete) photonic band gaps.[3] Moreover, photonic crystals made of inorganic semiconductors may require fewer layers to achieve the same level of attenuation when compared with silica or polystyrene. Wide band gap semiconductor colloids are ideal candidates for fabricating photonic crystals with band gaps in the optical regime because they exhibit lower absorption in the visible and near-IR region than narrow band gap semiconductors. Among wide band gap semiconductors, binary metal chalcogenides such as II−VI compounds have been widely studied because of their size-dependent luminescence[4] and other interesting properties such as thermoelectricity and photoelectricity.[5] Spherical colloids composed of these semiconductors also provide some physical and chemical properties that are not obtainable with dielectric materials such as silica and polystyrene. Several groups have reported the synthesis of spherical colloids from II−VI semiconductors (e.g., CdS and ZnS) through a homogeneous nucleation method or by coating silica or polymer beads with thin shells.[6] Despite these demonstrations, it is still necessary to achieve better control over the uniformity in the size and shape by developing new synthetic routes.

We recently demonstrated that monodispersed *a*-Se spherical colloids could serve as a new class of template to increase the diversity of semiconductor colloids.[7] Spherical Se@Ag_2-Se core−shell colloids with tunable shell thickness have been successfully synthesized by taking advantage of the high reactivity of *a*-Se toward silver.[8] Here we demonstrate that cation-exchange reactions could be employed to diversify the chemical composition of semiconductor colloids further. More specifically, we show that Se@Ag_2Se core−shell colloids could be transformed into Se@CdSe core−shell colloids through a cation-exchange reaction.

Ion-exchange reactions have been extensively studied in the general areas of catalysis and thin film technology.[9,10] A number of cations such as Ag^+, Sb^{3+}, Bi^{3+}, and Cu^+ have been used to replace Cd^{2+} in thin films made of CdSe and CdS.[10,11] An anion-exchange reaction has recently been used by Könenkamp and co-workers to transform columnar ZnO into tubular ZnS by exposure to H_2S gas.[11a] The resultant ZnS tubes could be further converted into Ag_2S, Bi_2S_3, and Cu_2S with preservation of the tubular shape through a cation-exchange reaction in an aqueous solution that contained the

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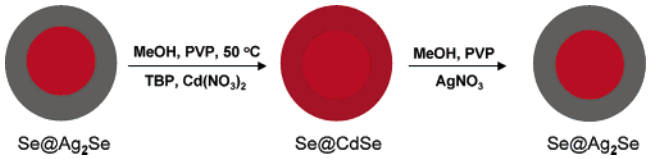
Scheme 1. Schematic Illustration Showing How $Se@Ag_2Se$ Core−Shell Spherical Colloids Were Transformed into $Se@CdSe$ Colloids with the Assistance of Tributylphosphine (TBP) at 50 °C[a]



[a] The $Se@CdSe$ colloids could be converted back into $Se@Ag_2Se$ by reacting with $AgNO_3$ at room temperature. Both reactions need the presence of poly(vinyl pyrrolidone) (PVP) as a stabilizer.

appropriate salt precursor.[11b] Most recently, Alivisatos and co-workers successfully demonstrated the use of a cation-exchange reaction between Ag^+ and Cd^{2+} to convert CdSe nanocrystals into Ag_2Se and vice versa.[12] Although the replacement of Cd^{2+} by Ag^+ is spontaneous because of the high mobility of Ag^+ and their large solubility product difference[13] ($K_{sp} = 3.1 \times 10^{-65}$ for Ag_2Se and $K_{sp}=1.0 \times 10^{-33}$ for CdSe), the replacement of Ag^+ by Cd^{2+} needs a small amount of tributylphosphine (TBP) and temperature elevation to facilitate the exchange process. In this communication, we demonstrate that these two cation-exchange reactions could be extended to the mesoscale system to prepare monodispersed spherical colloids that are very difficult to synthesize using conventional precipitation methods.

As shown in Scheme 1, the starting materials were $Se@Ag_2Se$ core−shell colloids that could be readily synthesized by reacting *a*-Se colloids with $AgNO_3$ at room temperature.[8] Methanol was used as the dispersion medium, and poly(vinyl pyrrolidone) (PVP) was added as a stabilizer to prevent possible agglomeration during the exchange process. For the conversion from Ag_2Se to CdSe, a small amount of TBP (less than 1 vol %, predissolved in methanol) was introduced into the colloidal suspension at 50 °C in the presence of excess Cd^{2+}. Phosphines have been commonly used as ligands in metal complex chemistry.[14] In particular, TBP can bind to Ag^+ cations on the surfaces of Ag_2Se shells to form intermediate complexes, facilitating the replacement of Ag^+ by Cd^{2+} at elevated temperatures. Once separated from the Ag_2Se shells, Ag^+ cations may exist in the form of L_4AgNO_3, L_3AgNO_3, or L_2AgNO_3 complexes (L = TBP).[15] In comparison, the conversion of CdSe to Ag_2Se could proceed spontaneously in the presence of excess Ag^+ at room temperature without the use of any catalyst or ligand.

We first used EDX to monitor the cation-exchange reaction between Ag^+ and Cd^{2+}. More specifically, $Se@Ag_2Se$ core−shell colloids with an outer diameter of 214 nm and a shell thickness of 21 nm were employed to study the exchange kinetics. After 20 μL of TBP (0.1% v/v, as calculated for the final mixture) had been introduced into a methanol suspension (20 mL) containing both $Se@Ag_2Se$ (0.1 g) and $Cd(NO_3)_2$ (1 g), 3 mL of solution was taken from the reaction mixture at 5, 15, 30, 60, and 120 min, quickly centrifuged, and washed four times with methanol. The reaction was terminated after 150 min, and the final product was also washed with methanol. Elemental analysis was performed

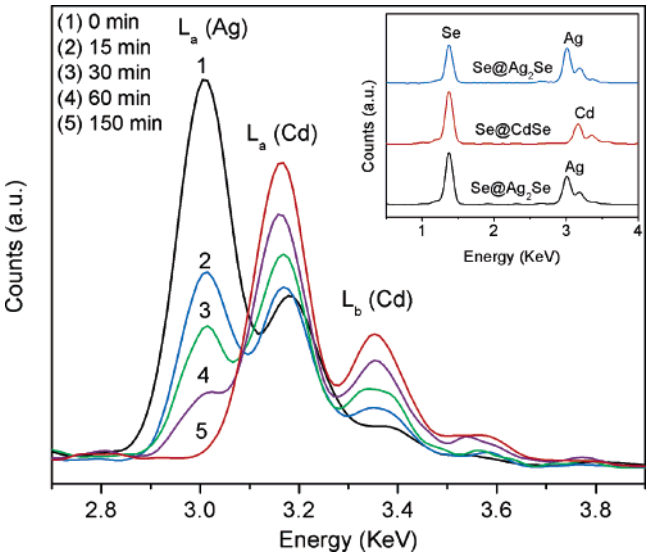


Figure 1. EDX spectra taken at various reaction times (after TBP introduction) confirm the gradual transformation of $Se@Ag_2Se$ into $Se@CdSe$. When the reaction time reached 150 min, the peak of Ag at 2.99 KeV disappeared and the peaks of Cd at 3.17 and 3.35 KeV showed up, implying the completion of transformation. The inset shows EDX spectra obtained from samples corresponding to three different stages outlined in Scheme 1: the $Se@Ag_2Se$ starting material (bottom), the $Se@CdSe$ product (middle), and the $Se@Ag_2Se$ product (top).

using EDX on these samples to analyze the degree of conversion. Figure 1 shows the EDX spectra, with peaks corresponding to the L shells of Ag and Cd. The peak of Ag monotonically decreased as the reaction time increased, and essentially no Ag was found for the sample taken at $t =$ 150 min. In comparison, the peaks of Cd steadily increased, implying the replacement of Ag^+ by Cd^{2+}. The reaction was fast in the early stage but gradually slowed as the conversion proceeded. This is because the in-and-out diffusion of Cd^{2+} and Ag^+ species in the shells has a profound influence on the reaction rate. The exchange reaction did not take place at room temperature even in the presence of TBP or at 50 °C without TBP. The conversion rate was also strongly dependent on the amount of TBP and the way that $Cd(NO_3)_2$ was added. When the amount of TBP was increased to 1% (v/v, as calculated for the reaction mixture), the conversion was remarkably retarded under the same condition. Even after 3 h of reaction, there still existed a small amount of Ag in the EDX spectrum, and no further progress for the reaction was detected at $t = 6$ h. In this case, higher concentrations of Cd^{2+} were needed to shift the reaction toward completion. The retardation of ion exchange might be caused by complex formation between the phosphine and Cd^{2+} although the mechanism is still not completely understood at the present time. In the presence of TBP (0.1% v/v, in the final mixture), it was also found that the stepwise addition of $Cd(NO_3)_2$—0.5 g at the beginning and an additional 0.5 g at $t = 30$ min instead of adding 1 g in one step at the beginning—could lead to complete conversion within 60 min. The second dose of $Cd(NO_3)_2$ is considered to provide fresh Cd^{2+} to speed up the ion-exchange process, and this observation also suggests the formation of complexes between phosphine and Cd^{2+}.

Although the conversion rate from Ag_2Se to CdSe was slow, the replacement of Cd^{2+} by Ag^+ could be completed in a few minutes at room temperature without adding TBP. This striking difference can be attributed to the lower solubility product of Ag_2Se relative to that of CdSe and the high mobility of Ag^+ in a solid lattice.[16] The inset of Figure 1 displays the EDX spectra of Se@Ag_2Se as the initial material (bottom), Se@CdSe after complete replacement of Ag^+ by Cd^{2+} (middle), and Se@Ag_2Se again after replacement of Cd^{2+} by Ag^+ (top). The atomic fractions of Ag in the initial Se@Ag_2Se colloids and Cd in the Se@CdSe colloids were 0.42 and 0.23, respectively. This result is consistent with the reaction stoichiometry in which every two Ag^+ cations were replaced by one Cd^{2+} cation. After the replacement of Cd^{2+} by Ag^+, the atomic fraction of Ag increased to 0.56, and the shell thickness also increased to 32 nm (as determined from the TEM image). This increase in silver can be attributed to the reaction between excess Ag^+ and *a*-Se cores, in addition to the replacement of Cd^{2+} by Ag^+ in the shells.

The colloidal samples shown in Figure 1 were also investigated by X-ray diffraction (XRD). As depicted in Figure 2, the XRD pattern taken from the as-synthesized Se@Ag_2Se colloids matched the orthorhombic lattice of β-Ag_2Se (lattice constants: $a = 4.33$ Å, $b = 7.06$ Å, and $c = 7.76$ Å), displaying no peak for the *a*-Se cores. CdSe peaks (indicated by the star symbols) appeared at $t = 15$ min and grew continuously as Ag^+ was replaced by Cd^{2+}. The XRD pattern at $t = 150$ min could be assigned to the wurtzite structure (hcp) (lattice constants: $a = 4.30$ Å, $b = 4.30$ Å, and $c = 7.01$ Å). The replacement of Cd^{2+} by Ag^+ restored the orthorhombic structure of Ag_2Se. On the basis of EDX and XRD results, it is clear that the partial conversion of Ag_2Se to CdSe led to the coexistence of CdSe wurtzite and Ag_2Se orthorhombic structures. A recent study showed that the partial replacement of O^{2-} by S^{2-} in ZnO columns of 200−300 nm diameter formed a thin (~10 nm) layer of ZnS at the surface.[11] Our observation suggests that a partial conversion of Ag_2Se to CdSe might form a multiwalled structure with Ag_2Se and CdSe as the inner and outer shells, respectively. We also examined the XRD patterns of Se@CdSe core−shell colloids with various shell thicknesses: 8, 12, and 21 nm. Figure S1 shows these XRD patterns, together with the pattern for solid CdSe colloids of 121 nm radius. For colloids with 8 nm and 12 nm thick shells, the (002) peak of the wurtzite lattice was predominant. In comparison, the (100) peak became comparable to the (002) peak for colloids with 21 nm thick shells and solid CdSe colloids.

Figure 3 shows scanning electron microscopy (SEM) images of all the samples shown in Figure 1, in addition to *a*-Se colloids. The insets are transmission electron microscopy (TEM) images of the same samples after the Se cores had been selectively removed with hydrazine hydrate. Note that the size uniformity, spherical shape, and surface smoothness were kept in all of these processes. The diameter of *a*-Se colloids was increased from 193 to 216 nm after they had been transformed into Se@Ag_2Se core−shell colloids.

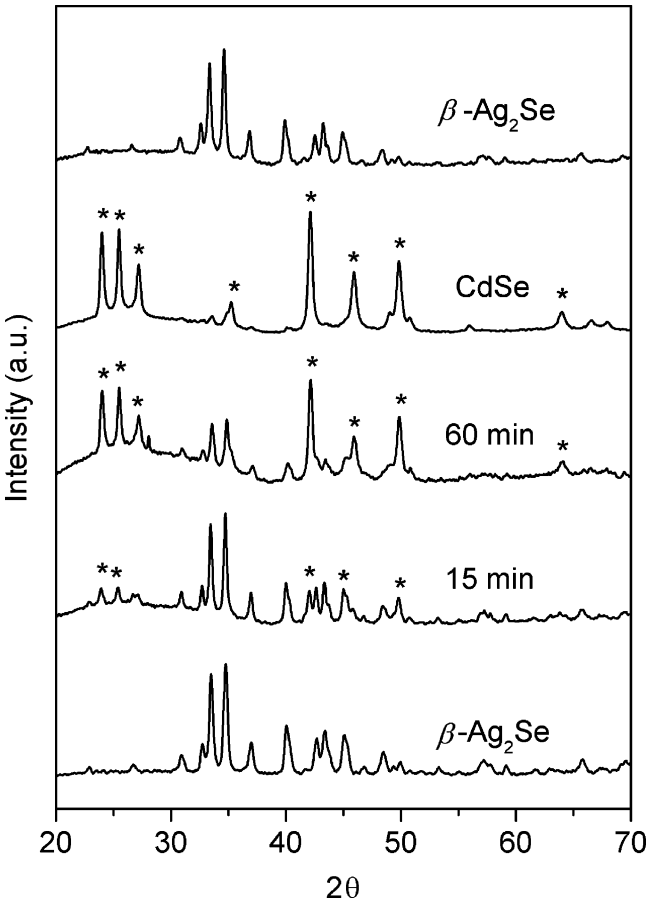


Figure 2. XRD patterns taken from samples at different stages of the cation-exhange reaction. Because the Se cores were amorphous in structure, the Se@Ag_2Se core−shell colloids (the bottom trace) showed only the diffraction pattern of orthorhombic β-Ag_2Se. As the reaction proceeded, the peaks of wurtzite CdSe became prominent (marked by the star symbol), and the peaks of β-Ag_2Se diminished in 150 min. After the CdSe shells were converted back into β-Ag_2Se, the orthorhombic structure of β-Ag_2Se was recovered again (top trace).

After the conversion of Ag_2Se shells to CdSe, the diameter of the colloids and the shell thickness were almost the same within the experimental error (214 nm). This is because the density of CdSe (5.67 g/cm^3) is relatively lower than that of Ag_2Se (8.40 g/cm^3), which can compensate for the decrease in mass and result in a negligible volume contraction for the shell (4%). For the replacement of Cd^{2+} by Ag^+, both the diameter and shell thickness of the colloids were slightly increased because of the additional reaction between Ag^+ and the *a*-Se cores.[8]

The spherical shape and monodispersity in size associated with the Se@CdSe core−shell colloids are immediately useful to the fabrication of photonic crystals. To this end, we have crystallized the Se@CdSe core−shell colloids shown in Figure 3C (214 nm in outer diameter and 21 nm in shell thickness) into 3D opaline lattices on glass substrates using a previously reported method.[17] The inset of Figure 4 shows the cross-sectional SEM image of a typical sample, which displays a face-centered cubic (fcc) structure with its (111) planes oriented parallel to the surface of the supporting substrate. Figure 4 shows the UV−visible reflection spectra

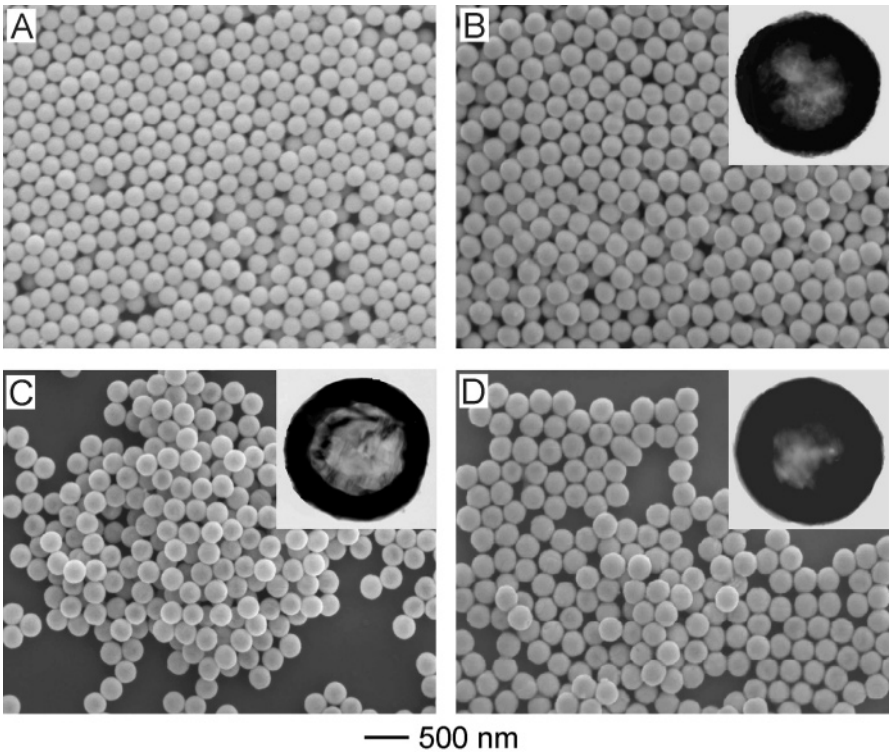


Figure 3. SEM images of (A) *a*-Se colloids; (B) Se@Ag_2Se core−shell colloids that served as the starting material for the ion-exchange reactions; (C) Se@CdSe colloids; and (D) Se@Ag_2Se colloids after the conversion of CdSe shells back into β-Ag_2Se. The insets show TEM images of the core−shell colloids after the *a*-Se cores had been selectively removed by dissolution with hydrazine hydrate.

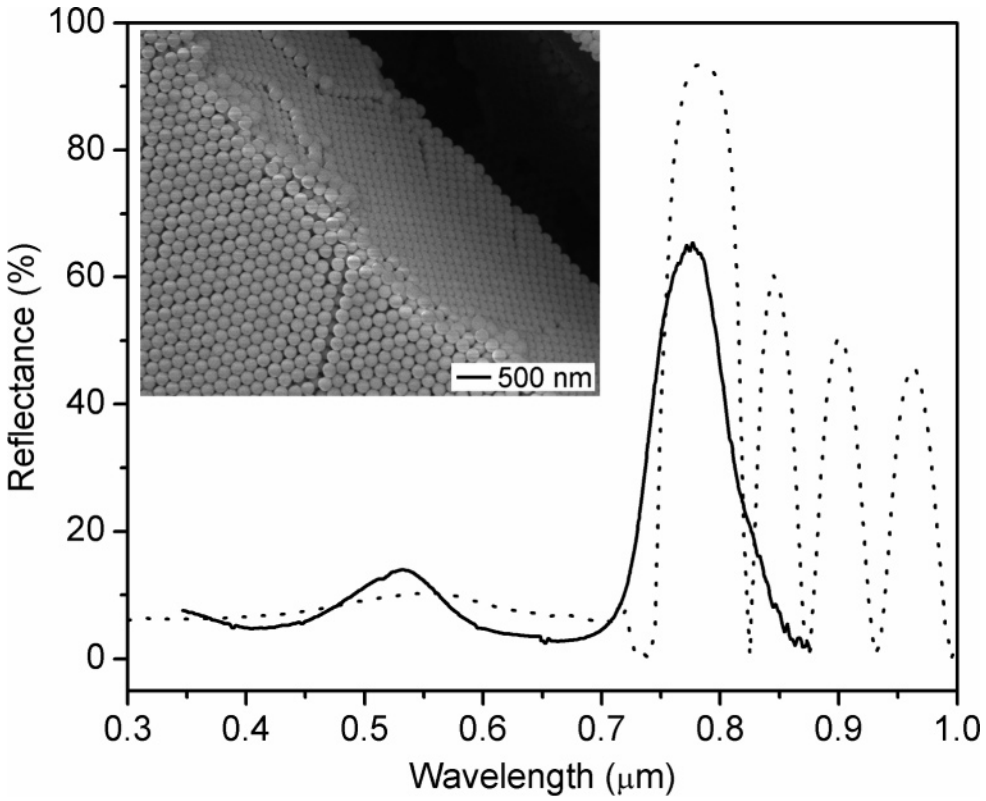


Figure 4. Reflection spectrum (solid line) taken from a 3D crystalline lattice assembled from Se@CdSe colloids of 214 nm outer diameter and 21 nm shell thickness. The dotted curve shows a spectrum calculated using the KKR model. The inset shows a cross-sectional SEM image of the crystalline lattice.

that were measured experimentally (solid curve) and calculated (dotted curve). In the experimental measurement, the incident light and detector were oriented perpendicular to the (111) planes of this lattice. For the calculation, the

Korringa−Kohn−Rostoker (KKR) method was used by assuming a thickness of 16 layers and a close-packing structure (26% air voids).[18] The dispersion curves of *a*-Se[19] and CdSe[20] are shown in Figure S2. The experimental result showed a relatively broad and strong peak around 775 nm, which can be assigned to the (111) diffraction according to the Bragg equation.[21] It is worth pointing out that the Se@CdSe core−shell colloids do not have absorption in this region. The calculated spectrum agreed with the experimental data, showing a strong stop band around 785 nm. The other peak around 556 nm in the calculated spectrum was much broader and less intense than the experimental data that is peaked around 533 nm. Note that the Se@CdSe core−shell colloids are strongly absorptive in this region. The oscillating pattern observed in the near-infrared region for the calculated spectrum is caused by interference because we assume that the sample had a thickness of only 16 layers.[22] Because the opaline lattice used for measurements was more than 100 layers thick, no interference pattern was observed experimentally. If the refractive index (n) and the volume fraction (X) were assumed to obey a linear relationship[23] ($n = n_{core} X_{core} + n_{shell}(1 - X_{core})$), then a simple calculation based on the Bragg equation gave a refractive index of 2.84 at 780 nm for the core−shell colloids. Here we assume that the volume fractions of the core and shell were 52 and 48%, respectively, and the refractive indices of CdSe and *a*-Se at 780 nm were 2.97 and 2.70. Because of the high contrast in refractive index, the stop band is much broader (80 vs 30 nm) than those typically obtained from opaline lattices made of polystyrene or silica spherical colloids at the same diameter of 214 nm.

In summary, we have demonstrated that cation-exchange reactions could be used to produce monodispersed spherical colloids made of II-VI semiconductors. More specifically, Se@CdSe core−shell colloids could be obtained by replacing the Ag^+ ions in Se@Ag_2Se colloids with Cd^{2+} in the presence of TBP at 50 °C. The CdSe shells had a wurtzite crystal structure and inherited the surface smoothness, spherical shape, and size monodispersity associated with the Se@Ag_2Se system. By taking advantage of the monodispersity of these core−shell spherical colloids, we have also assembled them into 3D crystalline lattices and have investigated their photonic properties through both experimental and computational studies. Because the *a*-Se colloids could be readily synthesized as monodispersed samples with diameters ranging from 100 to 400 nm, there should be no problem in tuning the stop band positions of these new photonic crystals in the entire visible and near-IR regions. Although photonic crystals assembled from spherical colloids have been studied for almost one decade, the materials have been largely limited to dielectrics such as silica and polymers. This limitation is mainly caused by the difficulty in synthesizing semiconductors as monodispersed spherical colloids. The present demonstration clearly provides a solution to this problem. This work focused only on CdSe because this semiconducting material is important for a variety of applications that range from luminscence[24] to the fabrication of photoconductors,[25] solar cells,[26] and thin film transistors.[27] It is expected that the ion-exchange approach will become a powerful route to monodispersed spherical colloids of semiconductors with a wealth of compositions and will allow us to probe the dependence of photonic band gap properties on the refractive index contrast experimentally.

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Supporting Information Available: Experimental procedures and materials, XRD patterns taken from Se@CdSe colloids with various thickness, and dispersion curves for *a*-Se and CdSe. This material is available free of charge via the Internet at http://pubs.acs.org.

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